

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **09-070533**

(43)Date of publication of application : **18.03.1997**

(51)Int.Cl. **B01J 23/20**
B01J 23/10
B01J 35/02
C01G 23/00
C01G 33/00

(21)Application number : **07-228739** (71)Applicant : **NIKON CORP**

(22)Date of filing : **06.09.1995** (72)Inventor : **TANAKA AKIRA**
SHINOHARA KIYOAKI
DOUMEN KAZUNARI

(54) PHOTOCATALYST

(57)Abstract:

PROBLEM TO BE SOLVED: To continuously and arbitrarily regulate the band gap of a compd. by using a specified oxide and producing one of hydrogen and oxygen by the photolysis of water.

SOLUTION: This photocatalyst is made of a compd. represented by the formula $A_2-xB_2C_3-xD_xO_{10}$ (where A is one or more kinds of elements selected from among alkali metals and hydrogen, B is one or more kinds of rare earth elements, C is one or more kinds of group IVa metallic elements, D is one or more kinds of group Va elements and $0 \leq x \leq 1$) and produces at least one of hydrogen and oxygen by the photolysis of water. Since the band gap of the compd. can be continuously varied in accordance with the value (x), a photocatalyst fit for conditions in use such as a used light source can be selected. The photocatalyst is, e.g. $Cs_2La_2Ti_3O_{10}$, $Cs_1.5La_2Ti_2.5Nb_0.5O_{10}$ or $CaLa_2Ti_2NbO_{10}$.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

* NOTICES *

JPO and NCIPPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] (General formula I) A2-xB2C3-xDxO10 (A is one sort or two sorts or more of elements chosen from alkali metals or hydrogen among a formula): B is one sort or two sorts or more of elements chosen from rare earth elements, and C is one sort or two sorts or more of elements chosen from 4A group metallic element. one sort or two sorts or more of elements with which D was chosen from 5A group metallic element -- it is -- x -- the numeric value of the arbitration of $0 \leq x \leq 1$ -- it is -- the light characterized by consisting of an oxide expressed -- water -- decomposing -- the photocatalyst of hydrogen and oxygen which makes either generate at least.

[Claim 2] Water is disassembled with the light characterized by for C in said general formula (I) being titanium, and D being niobium in a photocatalyst according to claim 1, and it is the photocatalyst of hydrogen and oxygen which makes either generate at least.

[Claim 3] In a photocatalyst according to claim 1, water is disassembled with the light characterized by B in said general formula (I) being a lanthanum, and it is the photocatalyst of hydrogen and oxygen which makes either generate at least.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. **** shows the word which can not be translated.

3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Belonging [invention] technical field] This invention relates to the photocatalyst which photodissociates water, and is used in case [of hydrogen and oxygen] either is made to generate at least.

[0002]

[Description of the Prior Art] In the present age, having utilized them effectively is mentioned to the background according to which we the human beings have built such advanced civilized society, using coal and petroleum which are a fossil resource as an energy source. And as current and an energy source, the petroleum which is a fossil resource, and the atomic energy (atomic energy) using the energy emitted with change of the proton and neutron which constitutes an atomic nucleus are used.

[0003] However, to the fossil resource, from the 80s, a close-up of a petroleum exhaustion problem is taken ignited by an oil crisis, and it began to debate earnestly. Moreover, after the 90s came, the global warming issue was raised as one of the environmental problems of an earth scale. CO₂ discharged as one of the causes of this global warming in case a fossil fuel is burned is mentioned. Thus, to the fossil resource, it has the problem from the both sides of an exhaustion problem and an environmental problem.

[0004] On the other hand, in spite of having made noise with the energy of a dream to atomic energy and having appeared, it is in the situation that social consensus is not yet obtained in safety. Therefore, recently in each country, construction of a new nuclear power plant is in a difficult situation. Moreover, the newspaper is full of stories about also about reprocessing of spent reactor fuel. Thus, about atomic energy, it can still be said from the feeling of fear to activity that it is an energy source with many problems socially.

[0005] Based on the above-mentioned thing, when considering energy problems with an environmental problem, it is thought that the hydrogen without discharge of CO₂ or emission of activity which is a clean energy source is useful. And it is a very natural result on this blue earth to ask water for this source of hydrogen. The chemical reaction which makes hydrogen generate from water, i.e., the decomposition reaction of water, is a reaction of a rise leech, and it needs a certain energy. If the thermal power station and nuclear electric power generation which used petroleum as the raw material as an energy source for the decomposition reaction of this water are used, it is putting the cart before the horse. That is, it is necessary to be the clean energy which, of course, has neither discharge of CO₂, nor emission of activity as an energy source used for the decomposition reaction of water, and it is the best to use light (for example, sunlight).

[0006] Although a water molecule must absorb light and must excite to the electronic state which carries out joint cleavage in order to advance the direct photolysis of water, for that purpose, the light energy of the vacuum-ultraviolet field of 165nm or less is required. Therefore, water is stable forever only by leaving it at a room temperature, and is. However, if the photocatalyst used as the driving force which causes a photolysis reaction is made to exist there, the decomposition reaction of water will advance, and the hydrogen or oxygen which is a product is generated.

[0007] If the light energy more than the band gap of the semi-conductor photocatalyst to be used is made to absorb, a hole will be formed in a valence band and electron will be formed in a conduction band,

respectively. A hole oxidizes water, oxygen is made to generate, and electron can return water and can make hydrogen generate. Thus, in the photocatalyst which can transform light energy into chemical energy, it is observed noting that an oxide with the layer structure shows especially high catalytic activity. For example, the oxide (JP,61-197033,A, JP,62-74452,A) of a single string represented by K4Nb 6O17 and its ion exchanger and a series of oxides (Japanese Patent Application No. 63-328516) represented by KCa2Nb 3O10 are known.

[0008] Since the photocatalyst of these layer structures can use between the layer as a place of the reaction of catalytic reaction compared with the photocatalyst of the shape of bulk without the layer structure, its surface area which can participate in a reaction is large, and it shows high catalytic activity. Furthermore, in an oxide with the layer structure, since the reducing substance and the quality of an oxide to the hole and electron which were produced in optical pumping exist in near, the migration length of a hole and electron becomes short, and the probability of the recombination of a hole and electron decreases. Therefore, the holes and electron which can participate in a reaction increase in number, and high catalytic activity is acquired.

[0009]

[Problem(s) to be Solved by the Invention] However, the presentation ratio of a configuration element is being fixed and the photocatalyst of these layer structures was not able to adjust a band gap to arbitration. Therefore, the photocatalyst which suited the use light source and which carries out band gap ** was not able to be used. So, it is in offering the photocatalyst of the layer structure which can make arbitration adjust a band gap continuously in this invention. That is, it is in offering the photocatalyst of the layer structure of the presentation system which can design easily the photocatalyst which has a band gap adapted to the operating wavelength of a photocatalyst.

[0010]

[Means for Solving the Problem] this invention persons are (general formula I) $A_2-xB_2C_3-xD_xO_{10}$ (among a formula) as a result of wholeheartedly research. : A is one sort or two sorts or more of elements chosen from alkali metals or hydrogen. B is one sort or two sorts or more of elements chosen from rare earth elements, and C is one sort or two sorts or more of elements chosen from 4A group metallic element: one sort or two sorts or more of elements with which D was chosen from 5A group metallic element -- it is -- x -- the numeric value of the arbitration of $0 \leq x \leq 1$ -- it is -- it finds out that the oxide (the first term of a patent claim) expressed is the photocatalyst which can adjust a band gap to arbitration, and came to accomplish this invention.

[0011]

[Embodiment of the Invention] it found out that this invention persons examined catalytic activity over the light of oxide expressed with a general formula (I), and a band gap changed continuously, and there were ***** in **. As a stratified compound in which the ion exchange is possible, the oxide expressed with a general formula (I) was not yet known about the physical properties over the light of these oxides, and the catalytic activity over light, although already shown in Journal of Materials Chemistry, 3,709-713, and (1993).

[0012] Balancing the amount of permutations can only **** carry out the part which permuted the element of C of oxide $A_2B_2C_3O_{10}$ of $x=0$ by the pentavalent element from the tetravalent element, and the amount of A, and the oxide expressed with the general formula (I) of this invention can consider them to be the oxide which is maintaining charge neutrality. A is a univalent element and is one or more elements specifically chosen from alkali metals (a lithium, sodium, a potassium, a rubidium, caesium) or hydrogen. A lanthanum is the most desirable although B is one sort or two sorts or more of elements chosen from rare earth elements. C is one sort or two sorts or more of elements chosen from 4A group metallic element, and titanium, a zirconium, etc. are specifically raised. Titanium is more effective than the photocatalyst activity is high especially as C especially. Although D is one sort or two sorts or more of elements chosen from 5A group metallic element, niobium, a tantalum, etc. are specifically applied. Especially niobium is an element desirable as D by the photocatalyst activity being high.

[0013] Moreover, the value of x can take the numeric value of the range of $0 \leq x \leq 1$, and can change the band gap of a compound continuously with the value. this invention persons found out this fact only after they measured that optical band gap. Thus, if the band gap of a photocatalyst can be adjusted, selection of the photocatalyst adapted to service conditions, such as the use light source, can be performed, and more efficient use can be performed. The element furthermore permuted is chosen or it

further becomes easy to carry out adjustment of a band gap by increasing the number of elements to permute.

[0014] Although the photocatalyst of this invention is compoundable by mixing salts, such as the oxide or carbonate of each metal component which becomes the usual solid phase technique, i.e., a raw material, and a nitrate, by the target presentation ratio, and calcinating at suitable temperature, even if it compounds by the other wet method or the gaseous-phase method, it is not cared about at all. Moreover, when A is hydrogen, the oxide of the general formula (I) whose A is alkali metal is compounded first, after that, by carrying out the ion exchange of this oxide in acid water solutions, such as a nitric acid, the ion exchange of the alkali metal of A is carried out to hydrogen, and it is compounded. Of course, even when A is alkali metal other than hydrogen, the target oxide can be similarly compounded by the ion exchange reaction. That is, it is compoundable with the ion exchange reaction of a hydrogen ion, alkali-metal ion, or alkali-metal ion.

[0015] Furthermore, if the rise of a manufacturing cost does not interfere, the usual qualification performed to the photocatalyst of this invention to photocatalysts which are co-catalysts, such as Pt and support of NiO, can be performed. Moreover, in a clay mineral, qualification for using effectively between the layers used as the reaction place of a photolysis reaction which is often performed can also be performed. That is, catalytic activity can be raised by building a column for between layers by an inorganic polykaryotic hydroxide ion etc. like a clay mineral, or extending the distance between layers by the ion exchange of alkylammonium.

[0016] In case the photocatalyst of this invention performs the photolysis reaction of water, it is not necessary to restrict water to pure water, and even if it uses sacrifice reagents, such as alcohol and complex ion, so that it may be well used for the photolysis reaction of common water, it may not interfere at all, and the photolysis reaction of the water with which salts, such as a carbonate and a hydrogencarbonate, were mixed may be performed. Although the example explained this invention concretely below, this invention was not restricted to this.

[0017]

[Example]

[Example 1]

(Adjustment of a photocatalyst) the inside of a series of compounds which are $Cs_2-xLa_2Ti_3-xNb_xO_{10}$, $x=0$, and 0 . -- the catalyst was compounded about 5 and 1.

[0018] Composition prepared the oxide or carbonate of each component by stoichiometry.

(1) $Cs_2La_2Ti_3O_{10}$ Weighing capacity of 3:14.62 g preparation Cs_2CO , $La_2O_3:14.62g$, and the $TiO_2:10.76g$ was carried out, respectively.

(2) $Cs_1.5La_2Ti_2.5Nb_0.5O_{10}$ Weighing capacity of 3:11.69 g preparation Cs_2CO , $La_2O_3:15.58g$, $TiO_2:9.55g$, and the $Nb_2O_5:3.18g$ was carried out, respectively.

(3) $CsLa_2Ti_2Nb_0O_{10}$ Weighing capacity of 3:8.34 g preparation Cs_2CO , $La_2O_3:16.68g$, $TiO_2:8.18g$, and the $Nb_2O_5:6.80g$ was carried out, respectively.

[0019] These (1) It ground after mixing a raw material about - (3), it put into the platinum crucible, and calcinated at 1200 degrees C in air for 10 hours. The mortar ground each sample after baking in particle size of 10 micrometers or less, respectively, and the obtained particle was identified according to the powder X diffraction. It checked that it was the compound which has the stratified perovskite structure made into the purpose from the result of a powder X diffraction. Moreover, it asked for the band gap of the these-compounded compound optically by measuring a diffuse reflectance spectrum. A measurement result is shown in Table 1.

(Evaluation of catalytic activity) Evaluation of the catalytic activity of a photocatalyst was performed by making hydrogen generate from the methanol water solution which added the methanol as a sacrifice reagent using closed circulatory system catalytic-reaction equipment.

[0020] 1g of photocatalysts and the support reagent (0.1wt(s)% of the photocatalyst chloroplatinic acid water solution containing corresponding platinum) which carried out [above-mentioned] preparation were put in into 400ml (water is 350ml and a methanol is 50ml) of methanol water solutions, and the high-pressure mercury lamp was irradiated from the interior, stirring with a magnetic stirrer within a reaction container. The coil used the thing made from Pyrex. The gas chromatography performed the detection and the quantum of hydrogen which were generated. A measurement result is shown in Table 1.

[Example 2]

(Preparation of a photocatalyst) The proton exchanger of the photocatalyst of (1) - (3) compounded in the example 1 was compounded.

[0021] Acid treatment for compounding a proton exchanger was performed by the following approaches. 5g of compounds of the caesium compounded in the example 1 was taken, and about (1) $x=0$, it stirred in 100ml of hydrochloric acids of 0.5 conventions, and stirred for three days in 100ml of nitric acids of five conventions about (2) $x=0.5$ and (3) $x=1$, and filtered water washing was carried out after that. The particle of the obtained proton exchanger was also identified according to the powder X diffraction as well as an example 1. It checked that it was the compound which has the stratified perovskite structure made into the purpose from the measurement result of a powder X diffraction. Moreover, it asked for the band gap of the these-compounded compound optically by measuring a diffuse reflectance spectrum. A measurement result is shown in Table 1.

(Evaluation of catalytic activity) Evaluation of the catalytic activity of a photocatalyst was performed by making hydrogen generate from the methanol water solution which added the methanol as a sacrifice reagent using closed circulatory system catalytic-reaction equipment.

[0022] 0.5g of photocatalysts and the support reagent (0.1wt(s)% of the photocatalyst chloroplatinic acid water solution containing corresponding platinum) which carried out [above-mentioned] preparation were put in into 400ml (water is 350ml and a methanol is 50ml) of methanol water solutions, and the high-pressure mercury lamp was irradiated from the interior, stirring with a magnetic stirrer within a reaction container. The coil used the thing made from Pyrex. The gas chromatography performed the detection and the quantum of hydrogen which were generated. A measurement result is shown in Table 1.

[0023]

[Table 1]

試料名	水素発生量 ($\mu\text{mo l}/\text{hr}$)	バンドギャップ (eV)
$\text{Cs}_2\text{La}_2\text{Ti}_3\text{O}_{10}$	27	3.55
$\text{Cs}_{1.5}\text{La}_2\text{Ti}_{2.5}\text{Nb}_{0.5}\text{O}_{10}$	1442	3.63
$\text{CsLa}_2\text{Ti}_2\text{NbO}_{10}$	230	3.73
$\text{H}_2\text{La}_2\text{Ti}_3\text{O}_{10}$	2233	3.45
$\text{H}_{1.5}\text{La}_2\text{Ti}_{2.5}\text{Nb}_{0.5}\text{O}_{10}$	1030	3.50
$\text{HLa}_2\text{Ti}_2\text{NbO}_{10}$	6042	3.61

[0024] As a result of composition, the band gap suited the increasing inclination as the amount of niobium increased. However, when seen about catalytic activity, the correlation was not seen between a band gap and catalytic activity.

[0025]

[Effect of the Invention] The oxide expressed with the general formula (I) of this invention is the photocatalyst which can adjust a band gap, photodissociates water, and even if there are little hydrogen and oxygen, it can make either generate as above. Since this oxide has the layer structure, it is easy to embellish between layers with approaches other than the ion exchange. Since catalytic activity is maintained even if it makes these oxides support noble metals, such as Pt, of course, even if it makes these noble metals support, it does not interfere at all.

[0026] Moreover, it does not matter at all even if it uses these photocatalysts for other chemical reactions instead of a decomposition reaction of water. For example, it is applicable also to the reduction reaction of the decomposition reaction metallurgy group ion of the organic substance.

[Translation done.]